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Silane and Other Adhesion Promoters in Adhesive Technology

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I. INTRODUCTION

It is axiomatic that the paramount property of an adhesive is adhesion to the substrate, but adhesion is also critical in the performance of surface coatings, which must adhere to protect and in obtaining optimum mechanical properties in particulate- and fiber-filled composites. Many surface preparation techniques have been employed to achieve high initial adhesion; these range from removal of surface contamination (solvent and vapor degreasing) to changes in substrate profile (grit blasting) to chemical modification (phosphating of steel, anodic treatments of aluminum). None of these methods solve the most critical problem in adhesion technology: that of the damaging effect of water on organic/inorganic bonds. Hydrolytic stability is essential in many technologies.

It has been shown by Walker that many types of organic coating lose up to 85% of their initial adhesion under water-soaked conditions [1], that adhesives show a marked loss of bond strength in water [2,3], and that glass-fiber-reinforced composites are readily degraded [4]. To improve the initial bond strength between adhesives and substrate, adhesion promoters may be used. These function by improving substrate wetting or by secondary bonding by van der Waals forces, dipole-dipole interactions, hydrogen bonding or acid-base reactions. Relatively weak forces in the range 5–8 kcal/mol are involved. If hydrolytic stability of the bond is to be achieved, use of a coupling agent that is capable of forming primary chemical bonds, 50–250 kcal/mol [5], is required. The important distinction here is that in the nature of the bond formed, only coupling agents form primary bonds and can therefore be expected to produce water-resistant bonding. A coupling agent is therefore defined as a compound capable of chemical reaction with both the polymer and the substrate, although there is some evidence that reaction with the polymer is not necessarily a prerequisite. It should be noted that a coupling agent can function as an adhesion promoter; the reverse is not true. Current views are that only a limited range of organometallic compounds are true coupling agents.

II. EVIDENCE FOR COUPLING ACTIVITY

Interfacial bonding studies have attracted the attention of many workers using a variety of spectroscopic techniques. Evidence for coupling activity has been demonstrated in the cases shown in Table 1.

III. MECHANISM OF ADHESION PROMOTION

Mechanistic theories of adhesion promotion have been described in detail by Rosen [11] with sole reference to silanes, but it is likely that many of the proposed theories apply equally well to coupling agents in general. The proposed mechanisms are described below.

A. Chemical Bond Theory

As applied to silanes, the theory postulates that trialkoxysilane groups chemically bond to silanols on the mineral substrate surface by reaction of the hydrolyzed alkoxy group forming interfacial bonds of 50–100 kcal/mol [12] to 50–250 kcal/mol [13]. The organofunctional groups of the silane bond chemically to the polymer molecules. Both reactions were considered to be essential if true coupling is to be achieved. Although originally postulated for silanes, it is equally applicable to other adhesion promoters, including titanates and zirconates. It has been pointed out that although covalent bonds may be formed between polymer and mineral surfaces, some covalent oxane bonds are easily hydrolyzed [12,14], and examples of hydrolytically stable bonding have been achieved in the absence of chemical reaction with the polymer [12,15].

B. Deformable Layer Theory

This theory postulates that the interface zone is plastic, allowing stresses between the polymer and mineral surfaces to self-relieve without bond rupture. Internal stresses are thus reduced. It has been suggested that in the case of a silane, the film is too thin to allow this [11]. However, it is possible that the presence of the coupling agent might cause preferential adsorption. Credence for this view is given by the number of

Table 1 Evidence for Coupling Activity

Bond	Coupling Agent/Substrate	Method ^a	Ref.
Si–O–Al	Silane/Al ₂ O ₃	FTIR	6
Cr–O–Al	Volan/aluminium	ESCA	7
Zr–O–Al	Zirconate/aluminium		8
Si–O–Fe	Silane/iron	SIMS	9
Si–O–Si	Silane/SiO ₂	NMR	10
Si–O–Pb	Silane/lead oxide	FTIR	11
Ti–O–Si	Titanate/SiO ₂	FTIR	6

^aFTIR, Fourier transform infrared; ESCA, electron spectroscopy for chemical analysis; SIMS, secondary-ion mass spectrometry; NMR, nuclear magnetic resonance.

workers who report that the amount of adhesion promoter used is critical and that excessive usage may result in adhesion failure [16,17].

C. Surface Wettability Theory

Erickson and Plueddemann suggest that particularly in filled systems, complete wetting of the mineral surface will improve adhesion by physical adsorption that would exceed the cohesive strength of the polymer. However, it is difficult to see how physical adsorption provides bond reinforcement when the polymer is in competition with water and possibly other weakly bonded surface layers, and where chemical bonding is also present [12].

D. Restrained Layer Theory

In effect, this theory postulates a chemical reaction between promoter, polymer, and mineral substrate as in the chemical bond theory but also suggests that the presence of a region of intermediate modulus between polymer and substrate which transfers stress from the high modulus surface to the relatively low modulus polymer. Adhesive technology has long recognized this principle in specially formulated primers for use when bonding rubbery polymers to metals.

E. Reversible Hydrolytic Bond Theory

Best regarded as a combination theory, it postulates the chemical reactions between coupling agent, substrate, and polymer of the chemical bond theory together with the rigid interface of the restrained layer theory and the plastic interface of the deformable layer theory. It allows for stress relaxation by the reversible breaking of stressed bonds without loss of adhesion in the presence of water. It also argues that when Si–O or Ti–O substrate bonds are broken by the intrusion of water, they may re-form with some recovery in adhesion. It is likely that hydrogen bonding is a particularly important aspect of this theory, especially in the case of silanes [18]. Recovery of adhesion between urethane and epoxide coatings and metal substrates on drying out after water immersion has been demonstrated by Walker [19–21]. It is now generally accepted that some silane coupling agents do not need to react with the polymer chemically to provide enhanced initial and wet adhesion [16,22].

F. Oxide Reinforcement

This theory postulates that a primary mechanism by which silane coupling agents improve initial and wet adhesion is by reaction with the oxide surface on a metal to increase the cohesive strength of the oxide [23] and certainly, in the case of aluminum oxide, increase the wet strength of the oxide by inhibiting hydration of the oxide [24]. This has the effect of causing any failure to occur in the new weakest layer (i.e., the adhesive or coating). This may also explain, in part, the differences in bond strength achieved with different coupling agents and different metals, as it may be the nature of the oxide film and the degree of reinforcement that varies rather than any intrinsic property of a particular metal–adhesion promoter combination.

It seems unlikely that any single theory can explain the mechanism of adhesion promotion for such diverse systems as particulate- and fiber-filled composites, surface

coatings, and adhesives applied to the complete range of metallic and other mineral substrates. Plueddemann opines that all theories of adhesion describe factors that are involved in bonding through silane coupling agents [16], and this view is likely to apply generally to the entire field of adhesion promotion.

G. Other Mechanisms

In addition to the stated theories of adhesion promotion, there are other mechanisms that may be both operative and important and are of general application.

1. Interpolymer Networks/Chain Tangling

It has been suggested that in the case of silane coupling agents, interdiffusion of siloxanol segments with polymer molecules may be a factor in bonding thermoplastic matrices. Interpenetrating polymer networks (IPNs) need not necessarily involve cross-linking of the silane or other coupling agent and the polymer matrix. Plueddemann expresses the view that to establish a strong interpenetrating boundary layer involves a tricky interplay of mechanical and chemical interreaction at the interface [16]. A similar mechanism has been suggested for titanates [17].

2. Acid–Base Reactions

A comprehensive account of acid–base reactions is covered in detail in volumes 4 (No. 4), 5, and 8 (1990) and volume 5 (No. 1) (1991) of the *Journal of Adhesion Science and Technology* and a detailed account is beyond the scope of this chapter. Since different metal oxides have different isoelectric points in water and may therefore be regarded as acidic or basic, addition of material having acidic properties to adhesives to be used on basic substrates, or basic materials for use on acidic substrates, may improve adhesion [25]. Work with epoxide and polyurethane coatings of similar composition to adhesives have shown them to be basic in nature; the pH of water-soaked surfaces from which they were stripped is known to be 8–10. The aminosilanes APES and AAMS are strongly basic and when applied to oxide surfaces having isoelectric points in the range 9.1 (Al^{3+}) to 12.0 (Fe^{2+}) may be expected to produce a basic surface. Neither silane could therefore be expected to enhance the adhesion of a basic polymer by an acid–base reaction, although both have been shown to improve the initial and wet adhesion of epoxides and urethanes. This is not to argue that acid–base reactions are unimportant in adhesion promotion technology.

IV. METHODS OF USE IN ADHESIVE TECHNOLOGY

In general, adhesion promoters may be used as pretreatments or as additives. In the former case the promoter is used either as a solution in a suitable solvent or solvent mixture or as a formulated primer [26]; in the latter case they may be incorporated into the adhesive in a self-bonding concept [25]. The technique of filter treatment can be regarded as representing both approaches, although there is no evidence of this being used in filled adhesive systems. There are advantages and disadvantages inherent in both approaches: the pretreatment method allows a specific adhesion promoter to be used on a specific substrate to obtain optimum adhesion but has the disadvantage of introducing a process that is not under the control of the manufacturer. In theory the

self-bonding additive concept is almost universally desirable, but in practice there are several critical parameters that need to be recognized, including potential polymer reactions, depletion by water, and shelf life. In adhesive technology as opposed to surface coating technology, the additive approach may not be as effective [27,28].

V. SILANES

Silanes of the general structure $R-Si(OR')_3$, where R is an organofunctional group and R' a hydrolyzable group, constitute the most technologically important group of adhesion promoters in use today and have a solid background of associated theory. Silane molecules are bifunctional, containing polar silanol groups and organofunctional groups capable of reaction with polymers. The range of silanes available commercially is large and continually expanding. Typical silane adhesion promoters are shown in Table 2. Other silanes that are attracting increasing interest are the fluoralkyl-functional silanes, the chemistry and uses of which have been reviewed extensively by Owen and Williams [29], cationic methacrylate, and cationic styryl silanes [30].

A. Silane Coupling Reactions

The reactions of interest in silane coupling are summarized below.

(a) Hydrolysis of the silane group:

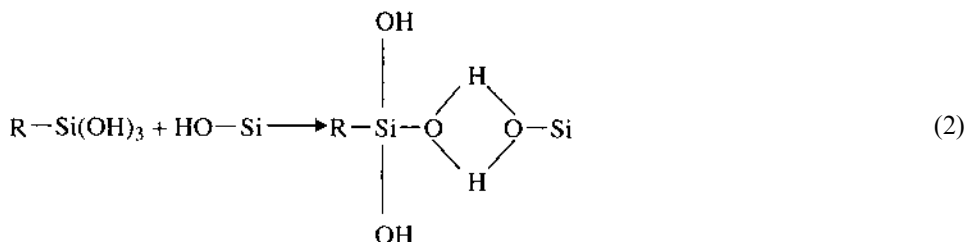


where HX is usually an alcohol.

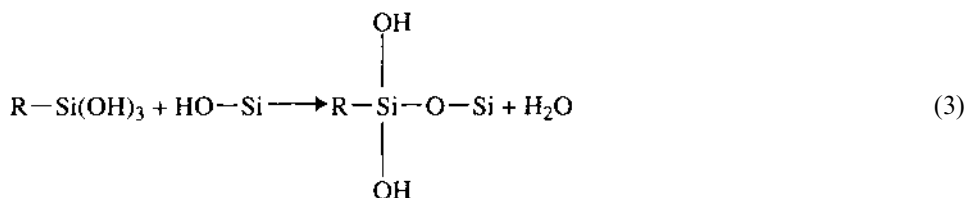
Table 2 Typical Silane Adhesion Promoters Commercially Available

Chemical Description	Structure	Functional Group	
		With Polymer	With Substrate
3-Chloropropyltrimethyl oxysilane	$ClCH_2CH_2CH_2Si(OCH_3)_3$	Chloro	Methoxy
Vinyltriethoxysilane	$CH_2=CHSi(OC_2H_5)_3$	Vinyl	Ethoxy
γ -Methylacryloxypropyl trimethoxysilane	$CH_2=C(\overset{\text{CH}_3}{\text{CH}})-\overset{\text{O}}{\parallel}C-OCH_2CH_2CH_2Si(OCH_3)_3$	Methacryloxy	Methoxy
γ -Glycidoxypropyl trimethoxysilane	$\text{CH}_2\text{CH}(\text{O})\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2Si(OCH_3)_3$	Aliphatic epoxide	Methoxy
γ -Mercaptopropyl trimethoxysilane	$HSCH_2CH_2CH_2Si(OCH_3)_3$	mercapto	Methoxy
γ -Aminopropyltriethoxy silane	$NH_2CH_2CH_2CH_2Si(OC_2H_5)_3$	Amino	Ethoxy
<i>N</i> - β -(Aminoethyl) aminopropyl trimethoxysilane	$NH_2CH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$	Amino diamino	Methoxy

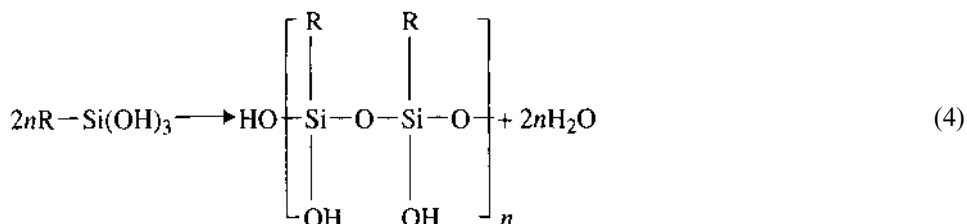
(b) Hydrogen bonding to the surface:



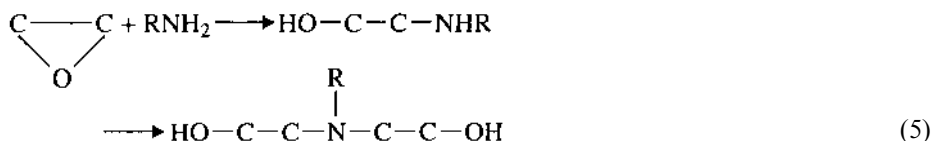
(c) Condensation with the surface:



(d) Polymerization:



(e) Reaction with the polymer:



In this case reaction of the primary amine group in an aminosilane with an epoxide group.

Hydrolysis, Eq. (1), may take place on the surface by reaction with surface water or in solution prior to application, occurring rapidly in neutral or slightly acidic water solutions and only slowly in hydrocarbon solvents [31]. Aminosilanes are autocatalytic and do not depend entirely on hydrolysis for aqueous solubility [32]. Polymerization, Eq. (4), may occur not only on the surface as the silane triols, $\text{RSi}(\text{OH})_3$, condense to form oligomeric siloxanes as in Eq. (3) via disiloxanols and trisiloxanols but also in solution before application. The speed at which this occurs and the oligomers become insoluble depends on silane concentration, solution pH, the presence of soluble catalytic salts [16], and the type of silane [33]. The pH factor is particularly important in silane technology.

The hydrolyzed silanol group will react with inorganic surface hydroxyl groups to form hydrogen bonds, Eq. (2), followed by condensation to form oxane bonds, Eq. (3). It should be noted that both hydrogen and oxane bond formation is reversible. Equation (5), reaction with the polymer, is a typical example of many possible reactions, depending on the functional groups on the silane and the polymer. In work with surface coatings,

Walker [34] has postulated a variety of possible chemical reactions between silanes and the functional groups present in epoxide and polyurethane compositions.

B. Nature of Silane Films on Metals and Glass

Bascom [35] employed a variety of techniques in his study of the structure of silane films deposited on glass and metal substrates and concluded that vinyl-, amino-, and chloro-functional silane films were deposited as polysiloxanes, some of which could easily be removed from the surface by organic solvents or water. Contact-angle measurements on the remaining strongly retained material indicated it to be of an open polymeric structure since it was easily penetrated by the wetting liquids. That the critical surface tension of a silane film is not an important factor in adhesion promotion by silanes is indicated by many measured values below the minimum Y_c value of about 35 dyn/cm for polyesters and 43 dyn/cm for epoxides for optimum wetting to occur [16]. It is suggested that on glass the performance of reactive silanes parallels reactivity rather than polarity (as described by the solubility parameters) of the organofunctional groups [36]. Plueddemann concludes that reactivity of the silane in copolymerization is much more significant than polarity or wettability [16].

Films deposited from nonpolar solvents are relatively thick ($>1000 \text{ \AA}$) and resistant to desorption; films from polar solvents are generally thinner ($<100 \text{ \AA}$) and easily disrupted by polar solvents. An adsorbed silane film can consist of different strata: a silane interface with covalent bonding [10], a relatively cross-linked intermediate layer, and a superimposed layer of relatively un-cross-linked material. In practice, adsorbed films on both glass and metals are discontinuous and consist of discrete islands or agglomerates, called the button-down theory [37].

The molecular structure of silane films has been shown to depend to a great extent on the pH of the solution from which it was deposited. Using modified infrared spectroscopy to examine films of γ -aminopropyltrimethoxysilane (APS) adsorbed on iron and aluminum surfaces, Boerio and Williams [38] demonstrated that the nature of the film was highly pH dependent. When deposited from solutions of pH below 9.5, the films were of the structure indicated by the expected interaction with oxides with the amine functional groups uppermost and available for reaction with the polymer. When the solution pH was greater than 9.5, the film structure was reversed, suggesting a reaction between the amino groups and the surface. In this case the organofunctional groups were not available for reaction with the polymer. Further, this upside-down structure resulted in less hydrolytically stable bonds.

In an investigation of epoxide joints on iron and titanium using γ -APS as a primer, Boerio [39] concluded that although the film structures formed by γ -APS adsorbed onto the two metals were very similar, the performance of the films as adhesion promoters was very different. He concluded that the performance was determined by the orientation of the APS molecules at the oxide surface rather than by the overall structure of the film. The orientation was determined by the isoelectric point of the oxide and the pH at which the films were adsorbed onto the oxide [39,40]. A comprehensive account of the structure of APS silane films is provided by Ishida and co-workers [41].

C. Performance of Silanes in Adhesive Technology

Boerio and co-workers [32,39] showed that the average shear stress of epoxide/titanium lapshear joints primed with γ -APS at either pH 10.4 or 8.0 showed almost no decrease in

strength after water immersion at 60°C for 60 days; unprimed controls lost 75% of their original strength. Epoxide/iron joints primed with APS at pH 8.0 retained 75% of their original strength after 60 days. Kaul and co-workers [24,42] investigated the strength of epoxide/aluminum single lapshear joints primed with γ -APS and showed that the use of γ -APS resulted in a lower dry bond strength than the unprimed control, and thicker films produced even lower bond strengths. The strength retention of unprimed joints after water immersion at 55°C was approximately 80% of the original, whereas the joints primed and standard dried (1 h at 25°C under vacuum) maintained only 50% of the dry strength. Joints primed and dehydrated (10 days at 110°C under vacuum) before bonding showed more than 95% retention.

In particularly useful paper, Gledhill and co-workers [43] investigated the effects of silane type, solution pH, solution age, and drying on the bond strength of a bisphenol A diglycidyl ether-based epoxide in a butt joint configuration. Several silanes were investigated. Unprimed joints showed a fall in bond strength from 37 to 5.8 MPa after 1500 h of immersion in water at 60°C. Joints treated with an aqueous 1% solution of γ -glycidoxypolytrimethoxysilane (GPMS) aged for periods up to 24 days before application showed a retained bond strength of between 17.5 and 34.4 after the same immersion time, with a peak retention between 30 and 90 min of aging. In a similar experiment using a solution of 95 parts of ethanol and 4 parts of water there was no solution age dependency, the recorded joint strengths were lower, and there was no evidence of increased water resistance. Attempts to accelerate the drying of the aqueous γ -GPMS film resulted in a marked reduction in bond strength. In a study of bismaleimide adhesives the same authors showed that the use of an aqueous solution of γ -APS increased the bond strength of the unprimed joint from 9.7 MPa–23 MPa, but was highly dependent on solution pH.

Kerr and Walker [28] investigated the bond strength of a two-pack polyamide-cured adhesive and a diphenylmethane diisocyanate-cured polyester adhesive on mild steel, stainless steel, and aluminum in a butt tensile configuration using a range of silanes as pretreatment primers and additives. It was shown that not all silanes were effective adhesion promoters on all substrates. The most effective silanes were γ -mercaptopropyltrimethoxysilane (MPS) on stainless and mild steel and *N*- β -(aminoethyl)- γ -aminopropyltrimethoxysilane (AAMS) on degreased aluminum and stainless steel, with the urethane, where a 20% improvement in bond strength was achieved. AAMS was the most effective on degreased aluminum with the epoxide. On grit-blasted substrates, considerably higher bond strengths were achieved. In the comparative trials all the silanes were found to be more effective when used as pretreatments rather than as additives, a finding directly opposed to that found in the case of surface coatings, where the opposite was true. It was considered that this was a function of viscosity and curing time. After exposure to 100% relative humidity for periods up to 2 years, stainless steel specimens coated with MPS and γ -GPMS showed an equilibrium bond strength retention more than double that of the uncoated controls. On glass the retention values were four to five times greater.

Hong and Boerio described a particularly interesting practical use of silanes in obtaining good adhesion to mineral oil-contaminated steel substrates [44]. They showed that the addition of 5 wt% of γ -GPMS to amidoamine-cured epoxide adhesives [Epon 828 and V115 (both Shell Chemical Co.)] to oil-contaminated mild steel lapshear specimens increased the initial bond strength from 968 psi to 1556 psi. More surprisingly, the specimens immersed in boiling water for 12 h increased to 1681 psi, whereas the nonsilane control decreased to 665 psi.

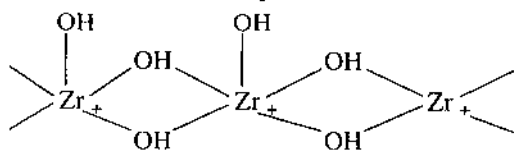
VI. ZIRCONATES

Organometallic compounds based on zirconium are actively being promoted as adhesion promoters and are claimed to function as coupling agents. Zirconium compounds appear to have widespread potential for use in the polymer industries since they exist in both water and organic solvent-soluble forms. The aqueous chemistry is dominated by hydrolysis, depending on zirconium and hydrogen ion concentration and the nature and concentration of anions present. Depending on the ligand present the polymeric species in solution can be cationic, anionic, or neutral [17]. Simplified structural representations of polymeric zirconium species are shown in Fig. 1

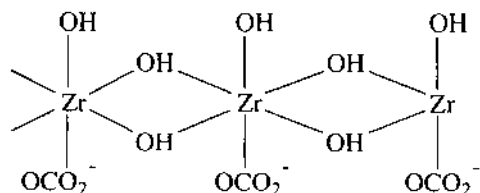
Solvent soluble compounds include zirconium acetylacetonate, zirconium methacrylate, and the family of neoalkoxyl zirconates. Some commercially available zirconates are shown in Table 3. Wang [8] has described the synthesis of a soluble linear Schiff base zirconium-based coordination polymer (*N*, *N'*, *N'''*, *N'''*-tetrasalicylidene-3,3'-diaminobenzidine) zirconium, and other hybrid copolymers, and has demonstrated improved adhesion on glass and aluminum substrates for poly(methyl methacrylate), polyethylene, and polypropylene when used as hot-melt compounds.

Studies on a reactive PVA copolymer (commercial vinyl alcohol), vinyl acetate copolymers stabilized by *N*-methylol acrylamide, and unreactive PVA homopolymer emulsions have shown that the resistance of these materials to cold- and boiling-water immersion tests can be improved considerably by the addition of zirconium oxychloride, zirconium-hydroxychloride, and zirconium-nitrate. These improvements in water resistance are considered to occur in the former cases by interaction between polynuclear

Cationic: zirconium oxychloride



Anionic: ammonium zirconium carbonate



Neutral: zirconium acetate

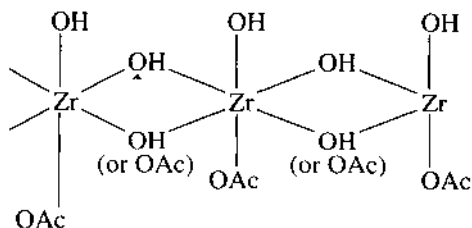
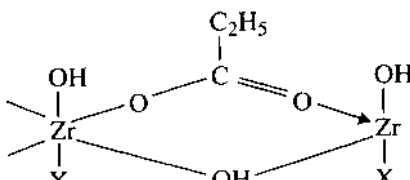


Figure 1 Structure representations of polymeric zirconium species.

Table 3 Typical Zirconate Coupling Agents

Chemical Description	Structure
Neoalkoxytris(neodecanoyl) zirconate	$\text{RO-Zr}\left[\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_9\text{H}_{19}\right]_3$
Neoalkoxytris(dodecanoyl)benzene sulfonyl zirconate	$\text{RO-Zr}\left[\text{O}-\overset{\text{O}}{\parallel}{\text{S}}-\text{C}_6\text{H}_4-\text{C}_{12}\text{H}_{25}\right]_3$
Neoalkoxytris(ethylenediaminoethyl) zirconate	$\text{RO-Zr}(\text{O}-\text{C}_2\text{H}_4-\text{NH}-\text{C}_2\text{H}_4-\text{NH}_2)_3$
Neoalkoxytris(<i>m</i> -aminophenyl) zirconate	$\text{RO-Zr}(\text{O}-\text{C}_6\text{H}_4-\text{NH}_2)_3$
Zirconium propionate	 $\text{X} = \text{OH} \text{ or } \text{O}_2\text{CC}_2\text{H}_5$

zirconium species and functional groups on the polymer and in the latter by reaction with the colloidal stabilizer. In these cases the zirconium compounds are functioning by an insolubilization process rather than as an adhesion promoter per se, but the end result is an increase in wet adhesion [45].

Other zirconium-containing coupling agents are the zircoaluminates, which are described in the technical literature [46] as inorganic polymer backbone materials of low molecular mass containing specific atom ratios of zirconium and aluminum with two organic ligands: one for overall molecular stability and the second to confer organo functionality; The commercial range includes amino-, carboxy-, and methacryloxy-functional compounds. It is claimed that the addition of these materials to adhesives and surface coatings improves their wet adhesion materially [47].

VII. TITANATES

A comprehensive patented range of titanates is marketed by Kenrich Petrochemicals, Inc. under the trade name Ken-React, and most of the published data on titanates emanates from this source. It is claimed that a typical titanate coupling agent provides six functions [17], although only three may be considered relevant to their use as adhesion promoters: the reaction of the alkoxy group of the titanate with free protons on the mineral surface to form an organic monomolecular layer on the substrate; transesterification resulting in cross-linking with carboxyl and hydroxyl groups in the polymer; and possibly chain entanglement. Titanate coupling agents are unique in that their reaction with free protons on the substrate surface results in a monomolecular layer

on the mineral surface whether it be filler particle or metallic substrate. The reaction proceeds according to the equation



where R'O is a hydrolyzable moiety. Cassidy and Yager [48] speculate that ester linkages are hydrolyzed and coordination or condensation occurs between the resulting hydroxyl groups and substrate surface groups. Calvert and co-workers [49] infer the presence of strong bonds between isopropoxytitanium tristearate and SiO_2 and Al_2O_3 by the failure to remove the coupling agent by an extended hot-water treatment.

X-ray photoelectron spectroscopy studies by Yang and co-workers [50] showed that aluminum and steel surfaces treated with di(dioctyl)pyrophosphate were covered with the titanate coupling agent, and in the case of steel, the octyl groups of the titanate molecule were uppermost, confirming the view that titanates modify hydrophilic metal oxide surfaces with a hydrophobic organic layer. The possibility has been raised that acidic surface sites on glass may catalyze condensation with surface silanols when chelate titanium acetyl acetonate is used [8]. The range of chemical types include monoalkoxy, chelate, coordinate, neoalkoxy, and cycloheteroatom. A very few of the wide range of commercial titanate coupling agents available are shown in Table 4.

Although there are many references to the improvement in adhesion of surface coatings obtained by the use of titanates, numerical data are sparse [51] and few are available on their use in conjunction with adhesives. The literature contains conflicting evidence on the value of titanate adhesion promoters, and in an investigation of eight titanates tested with an acrylic resin only two titanates performed better than the nontitanate control. It has been claimed that alkyl titanates are effective coupling agents for polyethylene [52–54]. Using isopropyl triisostearoyl titanate as a primer

Table 4 Typical Titanate Coupling Agents

Chemical Description	Structure	Type
Isopropyl tri(<i>N</i> -ethylaminoethylamino) titanate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{-CH-O-Ti(-O-C}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2)_3 \end{array}$	Monoalkoxy
Isopropyl triisostearoyl titanate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{-CH-O-Ti(-O-CCH}_{17}\text{H}_{35})_3 \end{array}$	Monoalkoxy
Titanium di(dioctylpyrophosphate)oxy acetate	$\begin{array}{c} \text{O} \\ \\ \text{C} \text{---} \text{O} \diagup \text{Ti} \left[\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{---O---P---O---P(OC}_8\text{H}_{17})_2 \\ \\ \text{OH} \end{array} \right]_2 \\ \\ \text{CH}_2\text{---O} \diagdown \end{array}$	Monoalkoxy
Tetraisopropyl di(dictylphosphito) titanate	$(\text{CH}_3\text{---CH---O---})_4\text{Ti} \left[\begin{array}{c} \text{O} \\ \\ \text{H---P(OC}_8\text{H}_{17})_2 \end{array} \right]$	Coordinate
Neoalkoxytri[<i>p</i> - <i>N</i> -(β-aminoethyl)amino phenyl] titanate	$\text{RO-Ti(OC}_6\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2)_3$	Neoalkoxy

for polyethylene/ Al_2O_3 joints, Sung and co-workers suggested that it was unlikely that this particular titanate functioned as an adhesion promoter in this system, notwithstanding the observation that heating the titanate above 70°C in vacuo resulted in a significant increase in peel strength [55].

Calvert and co-workers [49] have demonstrated the presence of isopropyl isostearate and isopropyl laurate in commercial isopropyl triisostearoyl titanate and conclude that this is the reason why the commercial product does not function as an adhesion promoter; treatment at 70°C in vacuo removes these fatty acid esters. It has been suggested to the author that failures to obtain improvements in adhesion using titanates can be remedied by isolating the pure compound (B. Nordenheim, private communication, 1988). It is possible that improvements in adhesion are more likely when commercial titanates are used as additives rather than as pretreatment primers.

It is only fair to say that the trade literature [17] is emphatic that it is critical to use the correct amount of titanate coupling agent. The use of excessive amounts is probably the most significant factor in application failure tests. It is strongly recommended that selected titanates should be examined in a range of concentrations from 0.1 to 2.0% by mass in a filled system and even lower for unfilled systems. Excess titanate will result in unreacted alkoxy groups on the surface and in a loss of adhesion of the polymer. This could lead to the mistaken conclusion that a particular titanate was unsuitable or even harmful.

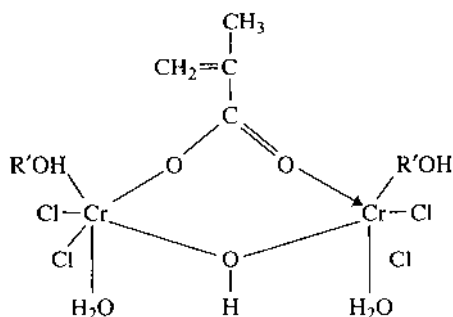
In general, titanates with the more polar organic moieties such as isopropyl tri(*N*-ethylenediamio)ethyl titanate and neoalkoxytri[*P*-*N*-(β -aminoethyl)amino phenyl] titanate are recommended for adhesion promotion to polar substrates. Titanates with relatively nonpolar moieties, such as aliphatic carboxy titanates and isopropyl tri(dioctylphosphato)titanate, will adhere better to the nonpolar substrates.

VIII. CHROMIUM-CONTAINING PROMOTERS

Adhesion promoters containing chromium fall into two main classes: inorganic and organic complexes. Examples of the former are the chromate conversion coatings used extensively in the aerospace industries for pretreatment of aluminum and its alloys. Although acting as anticorrosion coatings in their own right, they improve paint adhesion substantially [56]. Chromium conversion coatings that may be of chromium phosphate (amorphous, accelerated, or nonaccelerated) may be applied by brush dip or spray. The crystalline chromium phosphate type is normally restricted to steel surfaces. In a simulated sterilization test using epoxide can coatings on an aluminum surface, Paramonov and co-workers showed that the use of a chromate conversion coating was essential for satisfactory adhesion [57].

Examples of the organic type are the coordination complexes of trivalent chromium chloride with carboxylic acids (Volan manufactured by Du Pont). The methacrylate-chrome complex is well known in fiberglass technology. In water solution the chromium chlorides hydrolyze to form basic salts that form oligomeric salts through solvation of hydroxyl groups on the adjacent chromium molecules. Hydroxyl groups also bond to silanol groups on the glass surface via hydrogen bonding and possibly covalent oxane bonds. The organic acid group develops a fairly stable bond to chromium by being coordinated to adjacent chromium atoms [8]. Other chromium complexes of functional carboxylic acids have been proposed [58]. Following is a

typical structure:



A trivalent chromium fumarato-coordination compound, Volan 82, has been claimed to be an effective adhesion promoter for polyethylene coatings on aluminum. The toxicity of chromium compounds must place a question mark against their continued use as adhesion promoters.

IX. OTHER ADHESION PROMOTERS

In addition to the organometallic adhesion promoters, a large number of inorganic, organometallic, and organic compounds have been investigated, usually in specific adhesives and coatings or on selected substrates. A comprehensive account of coupling agents in use prior to 1969 is provided by Cassidy and Yager [48]. Although much of the reported information on other adhesion promoters concerns their use with surface coatings or filled systems, it is likely that many would also be suitable for use with adhesives and have therefore been included in the interests of completeness.

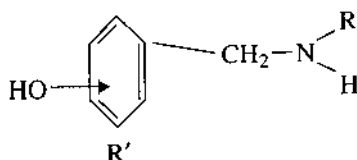
A. Phosphorus-Containing Compounds

Tritolyl phosphate (TTP) has been examined as a pretreatment for E-glass in epoxide laminates and thermoplastic adhesives for bonding poly(vinyl chloride) to aluminum, steel to zinc, and acrylonitrile-butadiene styrene to aluminum [59]. Mono- and diphenyl phosphate esters have been claimed to be suitable adhesion-promoting primers for acrylic adhesives on metal [60,61], unsaturated acid phosphates have been suggested as primers for use on metals to be bonded with free radical initiated adhesives [42], and thiophosphate esters have been suggested for adhesives to be used on plastics, ceramics, and metals [62].

B. Amines

Hydroxybenzamines of the general formula have been claimed to improve the adhesion of a wide range of coatings to zinc and cadmium and other metallic substrates when used as either pretreatment primers or additives [63]. Ethylenically unsaturated hydroxyfunctional amines have been claimed to improve the adhesion of water-based systems [64], and amines have been examined as adhesion promoters for aromatic isocyanate cured adhesives on glass and other substrates [65]. Primary aliphatic amines are claimed to improve the bondability of polyolefines [66] and an oxyethylated polyethylene

polyamine claimed for polymer-to-polymer bonding [67].



4-Ethylpiperidine has shown promise as an adhesion promoter [68], aminoethylpiperidine has been shown to be beneficial in steel-epoxide systems [48], and primers based on piperidine derivatives improve the adhesion of adhesives to aluminum and stainless steel [69]. Pyridene derivatives such as 2-(2-methylethyl)pyridene are claimed to be effective primers for crystalline and nonpolar polymers to be bonded with cyanoacrylate adhesives [70].

C. Organic Resins

A wide variety of organic resins have been claimed to act as adhesion promoters on many different substrates Mahajan and Ghatge have reported that the use of a liquid epoxide resin (epoxide equivalent 260) materially improved the initial adhesion of polysulfide sealants to anodized aluminum alloy [71]. Abietate-terminated polysulfide polymers, epoxide-terminated polysulfide polymers; and abietate-terminated polyesters have also been claimed to improve the adhesion of polysulfide sealants [72]. Oxygenated fluorocarbon primers are claimed to improve the bonding of polyacetal and polyamide-imide substrates [73]. A primer based on an ethylene-vinyl mercaptoacetate copolymer has been shown to improve the adhesion of epoxide adhesives to steel [74]. Primers containing diorganopolysiloxanes are claimed to improve the adhesion to silicone elastomers [75], and aromatic polyether resins with aminophosphonic acid groups are stated to improve the adhesive bonding of steel, galvanized iron, and aluminum [76].

D. Miscellaneous Promoters

DeNicola and Bell report the use of bibenzoylmethane and 1-(O-hydroxyphenyl)-3-phenyl-1,3-propanediol as wet adhesion promoters for epoxide resin adhesives on low-carbon mild steel [77]. Metal chelating O-hydroxybenzlamine compounds are stated to produce adhesion-promoting films on metals [78], and improved adhesion to titanium is claimed for metal alkoxide primers. Oxazolidines containing trialkoxy or triaryloxysilyl groups are claimed to be adhesion promoters on metallic substrates [79]. Improved adhesion of epoxide resin adhesives to copper substrates can be achieved by pretreatment in a weak solution of a benzoheterocyclic(thiol) compound [80] and benzotriazole and derivatives have been claimed to improve the bond between vinyl polymers and steel [81] and the adhesion of photosensitive compounds to polymeric substrates [82]. Pesetski and Aleksandrova describe the use of dicarboxylic acids as primers for polyamide films on copper [83].

X. EFFECTS OTHER THAN ADHESION PROMOTION

It should be noted that side effects are possible when using adhesion promoters/coupling agents as additives in adhesives and coatings, usually beneficial but not invariably so.

Beneficial effects from the use of titanates include deagglomeration, improved wetting, improved corrosion resistance, increased hydrophobicity, electrical conductivity in conducting systems, and acid resistance. The overall rheology of filled systems may be changed by both titanates and silanes requiring products to be reformulated. Silanes, particularly amino silanes, may function as curing agents or accelerators in epoxide and urethane adhesives, thereby reducing the pot life of a mixed system. These side effects should be considered in the selection or rejection of an adhesion promoter even if adhesion is the primary concern.

XI. CONCLUSIONS

In attempting to cover such a wide and diverse topic as adhesion promoters in a short chapter, the author is aware of many gaps in the information presented and the omission of many aspects of theoretical and practical interest; it is hoped that the references quoted will fill many of these gaps. It has been demonstrated that adhesion promoters/coupling agents have a major role to play in the development of adhesive technology, but only if due regard is paid to the importance of matching the promoter to the substrate and the polymer, pH effects, solution age, dosage, and film thickness. Plueddemann concludes that the performance of coupling agents may depend as much on the physical properties resulting from the method of application as on the chemistry involved.

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